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AIR RESOURCES BOARD

Report for the Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Grass Valley, CA Summer 2004

Prepared by
Operations Planning and Assessment Section
Quality Management Branch
Monitoring and Laboratory Division

June 9, 2005

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Monitoring Report Approval

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Executive Summary

Report for the Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Grass Valley, CA – Summer 2004

This report presents air monitoring results during fumigation of a home using the pesticides sulfuryl fluoride and chloropicrin. The monitoring was conducted at the request of the Department of Pesticide Regulation (DPR) to support their toxic air contaminant identification program. The testing occurred in Nevada County, from July 18 through July 24, 2004, around the sulfuryl fluoride fumigation of an approximately 81,000 cubic foot house. The product label for sulfuryl fluoride (Vikane®) requires that chloropicrin be used as a warning agent (lachrymator) during the fumigation. The study was conducted during the fumigation for powderpost beetles. Powderpost beetle fumigation requires a higher concentration of sulfuryl fluoride relative to other types of fumigation using this pesticide.

Structural fumigations in California consist, in general, of the following steps:

- 1. Sealing the structure with tarps.
- Introduction of the fumigant gas (and warning agent).
- 3. Exposure period (normally from 36 to 72 hours for powderpost beetle).
- 4. First opening of the tarp seal. This is referred to as the "mechanical vent." The purpose of the mechanical venting is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. A fan is used to pull the gas from the structure for release through a vent pipe near the eaves. This vent process generally lasts from 10 to 30 minutes and is followed immediately by the removal of the tarps. For the purposes of this monitoring study, the "mechanical vent" period has been defined as ending and aeration as starting when the tarps are completely removed.
- 5. Aeration (minimum of eight hours in California).
- 6. Clearing; a verification that sulfuryl fluoride concentrations are less than 5 ppmv inside the structure. This allows the structure to be re-occupied.

Per DPR recommendations, the test consisted primarily of sampling at multiple sites (12) around the structure at distances ranging from 5 feet to 40 feet from the structure and sampling inside after the house was cleared. Samples were collected based on the following schedule:

- 1. A 24-hour background at four sites (i.e., collected prior to the fumigation).
- 2. During fumigant introduction and the exposure period. This sampling was divided into daytime and overnight periods.
- 3. During the "mechanical vent" period.
- 4. During aeration. This sampling was divided into daytime and overnight periods.
- Post aeration and indoor sampling.

Samples were collected for a total of 14 periods. Two additional samplers were used at downwind locations during the mechanical vent period as ambient sulfuryl fluoride concentrations were expected to be the highest during this part of the process.

Sulfuryl Fluoride

The outdoor sulfuryl fluoride results ranged from less than the method detection limit (<MDL) to 100,000 ug/m³ (24,000 ppbv). The highest outdoor concentration was observed at a sampling site on the opposite side of the house but downwind from the mechanical vent during the mechanical vent sampling period (period eight). The test results are shown in a bar graph included in this Executive Summary.

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable levels greater than the estimated quantitation limit (>EQL) were also observed during all of the fumigation exposure periods. Four samples had quantifiable results during the first aeration sampling period (period nine) and only one sample had a quantifiable level observed during the remaining aeration periods (periods ten through thirteen).

All test results reported as "detected" (>MDL but less than the EQL) are questionable due to low level fluoride contamination in the sampling cartridges. Quantifiable levels (i.e., >EQL) are not considered affected.

We collected 179 samples for sulfuryl fluoride (including four background samples and 13 collocated samples). Of those, 35 percent (63 samples) were found to have quantifiable concentrations above the EQL, 38 percent (68 samples) were "detected," 26 percent (46 samples) were <MDL, and one percent (two samples) were invalid (log #s 30 and 145).

The sulfuryl fluoride results from three of the background samples were <MDL and the north site was "detected." The background results are not included on the following bar graph.

Two sequential 24-hour samples were collected inside the house at two locations (north and south ends of the first floor) after the end of the 20-hour aeration period. The sulfuryl fluoride results of the north inside sampler were 1600 ug/m³ (390 ppbv) and 750 ug/m³ (180 ppbv), respectively, for the two sequential 24-hour samples. The sulfuryl fluoride results of the south inside sampler were 2400 ug/m³ (570 ppbv) and 1100 ug/m³ (270 ppbv), respectively, for the two sequential 24-hour samples.

Chloropicrin

The outdoor chloropicrin results ranged from <MDL to 43,000 ng/m³ (5600 pptv). The highest outdoor concentration was observed at a sampling site on the opposite side of the house but downwind from the mechanical vent during the mechanical vent sampling period (Period eight). This site and sampling period also had the highest level of sulfuryl fluoride. The test results are shown in a bar graph included in this Executive Summary.

In general, the highest outdoor concentrations were observed during the mechanical vent period. Quantifiable results (>EQL) were observed during all of the fumigation exposure periods. A total of four samples had quantifiable results during the first two aeration sampling periods (periods six and seven) and no quantifiable levels were observed during the remaining aeration periods (eight and nine). The test results are shown in a bar graph included in this Executive Summary.

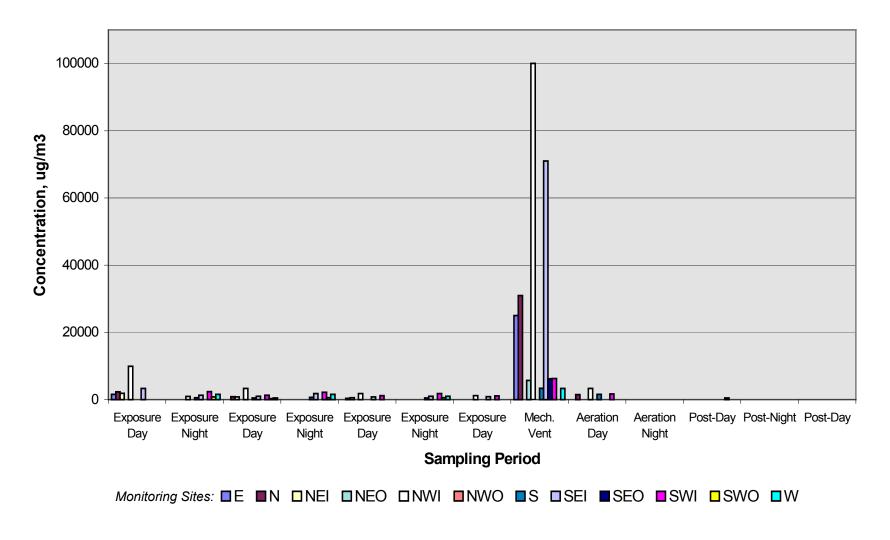
We collected 179 samples for chloropicrin (includes four background samples and nine collocated samples). Of those, fifty-four percent (97) were found to have quantifiable concentrations above the EQL, twenty-four percent (43) were "detected," twenty-one percent (38) were <MDL and one sample was invalid.

The chloropicrin results from the four background samples were all <MDL. The background period results are not included on the following bar graph.

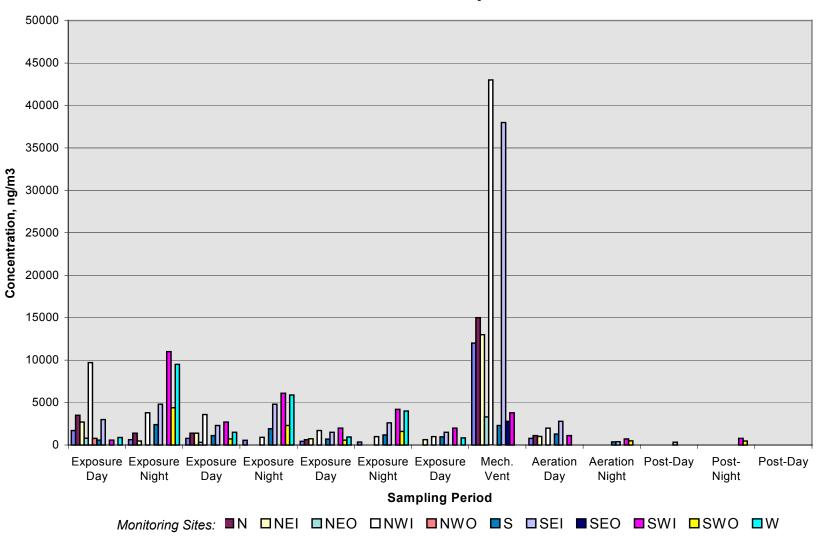
Two sequential 24-hour samples were collected inside the house at two locations (north and south ends of the first floor) after the end of the aeration period. The chloropicrin results of the north inside sampler were 72,000 ng/m³ (11,000 pptv) and 47,000 ng/m³ (7,100 pptv), respectively, for the two sequential 24-hour samples. The chloropicrin results of the south inside sampler were 83,000 ng/m³ (12,000 pptv) and 53,000 ng/m³ (7,900 pptv), respectively, for the two sequential 24-hour samples.

It should be noted that these indoor concentrations of chloropicrin following aeration were higher than were measured outdoors during mechanical venting. It should also be noted that the acute (1-hour) reference exposure level established by the Office of Environmental Health Hazard Assessment (OEHHA) for chloropicrin is 29,000 ng/m3 (toxicity endpoint is mild eye and respiratory irritation).

Sulfuryl Fluoride Outdoor Results 2004 Grass Valley Test



Chloropicrin Outdoor Results 2004 Grass Valley Test



Acknowledgments

Staff of the Special Purpose Monitoring Section collected the samples. Steve Rider coordinated the field work. Jim Omand and Michael Orbanosky of the ARB Special Analysis Section laboratory performed the method development and chemical analyses. Lynn Baker of the ARB Stationary Source Division provided comments on the monitoring protocol and report.

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Report for the Air Monitoring Around a Structural Application of Sulfuryl Fluoride in Grass Valley, CA - Summer 2004

I. <u>Introduction</u>

At the request of the California Department of Pesticide Regulation (DPR) (October 17, 2003, Memorandum, Helliker to Lloyd, and April 15, 2004, Memorandum, Sanders to Cook), the Air Resources Board (ARB) staff conducted pesticide air monitoring to determine concentrations of sulfuryl fluoride and chloropicrin during a structural application. This monitoring was done to fulfill the requirements of Assembly Bill 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. Similar monitoring was conducted earlier in the summer of 2004 in Loomis, California.

Grass Valley monitoring was conducted in Nevada County, from July 18 through July 24, 2004, around a sulfuryl fluoride fumigation of an approximately 81,000 cubic foot house. The product label for sulfuryl fluoride (Vikane®) requires that chloropicrin be used as a warning agent (lachrymator) during the fumigation. The study was conducted around a fumigation for powderpost beetles, which requires an elevated level of fumigant relative to structural fumigation for other pests (e.g., termites).

The sampling and analysis followed the procedures outlined in 1) the monitoring protocol (see page 1 of the separate Volume of Appendices), 2) the quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version), 3) the "Standard Operating Procedure for the Determination of Sulfuryl Fluoride Measured as Fluoride by Ion Chromatography" (page 12 of the Appendices), and 4) the "Standard Operating Procedure, Sampling, and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector," (page 19 of Appendices).

II. Fumigation Process and Test Overview

In general, structural fumigations in California consist of the following steps:

- 1. Sealing the structure with tarps.
- 2. Introduction of the fumigant gas (and warning agent).
- Exposure period.
- 4. First opening of the tarp seal. This is referred to as the "mechanical vent." The purpose of the mechanical venting is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. A fan is used to pull the gas from the structure for release through a vent pipe near the eaves. This vent process generally lasts from 10 to 30 minutes and is followed immediately by the removal of the tarps. For this

- monitoring study, the "mechanical vent" period has been defined as ending and aeration as starting when the tarps are completely removed.
- 5. Aeration (minimum of eight hours in California).
- 6. Clearing; a verification that sulfuryl fluoride concentrations are less than 5 ppmv inside the structure. This allows the structure to be re-occupied.

Per DPR recommendations, the test consisted primarily of sampling at multiple sites around the structure at distances ranging from 5 feet to 40 feet from the structure. Samples were collected based on the following schedule.

- 1. A 24-hour background at four sites (i.e., collected prior to the fumigation).
- 2. During fumigant introduction and the exposure period. This sampling was divided into daytime and overnight periods.
- 3. During the "mechanical vent" period.
- 4. During aeration. This sampling was divided into daytime and overnight periods.
- 5. Post Aeration. This sampling was divided into daytime and overnight periods.

The study included the background sampling period at four positions outside the house and 13 fumigation/post-fumigation sampling periods at 12 positions (1 collocated) outside the house. Samples were also collected at two additional positions outside the house for the mechanical vent (period 5) sampling period. Two sequential 24-hour indoor samples were collected at two locations after the house was "cleared."

III. <u>Fumigation Monitoring</u>

A single-family house in Grass Valley, California, was chosen for the fumigation monitoring site. Refer to Figure 1 for a rough map of the site and to Figure 2 for a more detailed diagram of the site. Refer to Appendix IV (page 77 of Appendices) for a copy of the fumigation log.

Fumigation Site, Application Rate, and Fumigation Information

The DPR's monitoring recommendation (April 15, 2004, memo, Sanders to Cook,) indicated the following:

"The application dosage of sulfuryl fluoride can vary, for a typical single-family house fumigation, from 6 - 16 ounces per 1,000 cubic feet for termites to a higher application rate necessary to control Powderpost beetle." It further indicated "The label rate for chloropicrin use as a "warning agent" is one ounce per 10,000 cubic feet of space to be fumigated."

"DPR recommends selecting a site with a volume of at least 26,000 cubic feet, no obstructions between the samplers and the structure, and an exposure time of at least 36 hours but no more than 48 hours that will be treated for the Powderpost beetle to assure a higher application rate."

Table 1 summarizes the actual application conditions and information.

Table 1 Fumigation Information

Location: 13016 Somerset Drive, Grass Valley, CA

Type of Structure: Two story House

Size of Structure: Approximately 81,000 cubic feet

Applicator: Norcal Pest Control
Pest Controlled: Powderpost Beetle
Product Applied: Vikane®, chloropicrin
Type of Application: Structural, tarped

Application Rate: 202 lbs. Vikane® initial; 40 oz./1000 ft.³

(crawl space, clay under-seal, no vapor barrier)

6 oz. chloropicrin total

Duration of Fumigation: 71 hours (amount of Vikane® was calculated assuming 72-

hour duration)

Duration of Vent 83 minutes (including tarp removal)

Duration of Aeration: Approx. 72 hours due to the holiday weekend Terminal Reading: 26 oz. Vikane®/1000 ft³ at 11:50 on 7/22/04

Method of Introduction: Vikane® is released into the structure as a gas via a leak-

proof tube and disbursed using one or more fans with a minimum capacity of 1000 cubic feet per minute for each pound of Vikane® released per minute. Chloropicrin, when used as a warning agent during structural fumigation with Vikane®, is applied in liquid form within structures five to ten minutes prior to fumigation. Chloropicrin is dispensed into a shallow plastic or non-aluminum metal pan with a wicking agent (e.g., cotton) and is placed in the direct air stream of a

fan to hasten evaporation.

Exposure Period: The fumigation process for powderpost beetles was expected to consist of a 36 to 72 hour exposure period. The intention of this study was to target a fumigation using a shorter exposure period (i.e., 36 hours rather than 72 hours) as higher Vikane® application rates are required to meet the 10x fumigation ounce hours. However, the standard practice of the company conducting the fumigation was to use an exposure period of 72 hours for powderpost beetles. As explained below, the amount of Vikane® used for this fumigation can still be considered as a "higher application rate."

Several other variables that affect the dose rate are 1) whether the fumigation is "monitored" (sulfuryl fluoride concentrations in the structure are monitored during the fumigation), 2) whether the foundation is a concrete slab or a raised floor over soil (crawl space), 3) if a crawl space, whether the soil is covered with a vapor barrier (plastic sheet), 4) if a crawl space and no vapor barrier is used, what type of soil makes up the "under seal." The Vikane® application rate, as calculated with the "Fumiguide,"

increases if 1) the fumigation is not "monitored," 2) there is a crawl space, 3) if the soil in the crawl space is not covered with a vapor barrier and, 4) for certain types of soil. For this study, the structure had a crawl space, no vapor barrier was used and the soil was identified as clay.

The company conducting the fumigation used an application rate of 2.5 pounds Vikane® per 1000 cubic feet (202.5 pounds for the 81,000 cubic foot structure). Apparently this rate was based on experience rather than on a strict use of the "Fumiguide." The fumigation log (Appendix, page 77) lists that the fumigation was "monitored," but the rate used was very close to the amount of Vikane® calculated by the "Fumiguide," 205 pounds total, if the fumigation was not "monitored." Although not the company's normal practice, in response to a request by ARB staff the company did take an initial and a terminal measurement. No measurement was taken during the fumigation.

The Vikane® application rate used for this test reflects a calculation based on a structure with a crawl space where no vapor barrier was used and a fumigation that was not "monitored." Those conditions required an amount of sulfuryl fluoride close to the amount that would have been required for a fumigation of this structure using a shorter exposure time (e.g., 36 hours) if a vapor barrier had been used in the crawl space and the fumigation had been "monitored."

Mechanical Vent Period: The "mechanical vent" period is a short aeration conducted at the end of the exposure period just prior to removal of the tarps. The purpose of the mechanical venting is to remove the gas between the tarp and the structure to minimize occupational exposure during removal of the tarps. A fan is used to pull the gas from between the tarp and the structure for release out a small vent pipe, pulled through at a tarp seam, usually located at approximately the height of the roof overhang. For this study, the mechanical vent sampling period included the time during removal of the tarp covering the structure. Referring to Figure 1, the mechanical vent was located on the south side of the structure (on the west side of the garage doors).

The time required for mechanical venting and tarp removal was 83 minutes. The mechanical venting started at 1220 (PST) and after approximately 40 minutes the crew began removing the tarps. The tarp removal was completed by 1343. Due the length of time required for sample change-out, this sampling period was actually somewhat longer and start/stop times do not exactly correspond to the start/stop of the mechanical vent process. The sampler start times for this period ranged from 1145 to 1215 and the end times ranged from 1326 to 1349 for an average sampling time of approximately 95 minutes.

<u>Aeration Period:</u> For the purpose of this study, aeration was defined as starting when the tarps were completely removed. The aeration period required by the product label is a minimum of eight hours. However, fumigation companies may choose to aerate the structure for a longer period of time, e.g., up to 48 hours. In any case, a fumigated structure cannot be reentered until it is "cleared" as having Vikane® concentrations of

less than five parts per million by volume (ppmv). The fumigator uses a Miran or Interscan gas analyzer to measure the Vikane® concentration to clear the structure for reentry.

The intention of this study was to target a fumigation using a 24-hour aeration period (i.e., re-entry would be cleared and post aeration sampling would begin after twenty-four hours of aeration). For this test, aeration started at 1343 on 7/22/04 and ended at approximately 0930 on 7/23/04, a duration of approximately 19.75 hours. After the house was cleared two samplers were placed inside the house, at opposite ends on the first floor, and sampling was started at 0959.

Sampling Locations

The DPR's monitoring recommendation (April 15, 2004, memo, Sanders to Cook) directed the following:

"The structure selected for monitoring must have enough clearance surrounding it to allow for sampler placement at a distance of 5 and 10 feet from the edge of the structure. Four background samples should be taken prior to application. Twelve samplers should be placed surrounding the structure as 3 rings. The first ring consists of four samplers located at the middle of and 5 feet from each side of the structure. The second ring consists of four samplers 10 feet out from each corner of the structure. The third ring contains four samplers which would be placed 30 to 50 feet from each side or corner of the structure. A thirteenth sampler will be collocated with one sampler in the first ring and at the site expected to be downwind during aeration. The collocated sample will be collected at this site during each sampling interval. Sample intake should be 1.5 to 2.0 meters above the ground. There should be no large obstructions between the structure and the furthest samplers."

Table 2 below lists the sampling sites and Figure 1 shows a rough map of the locations.

Table 2 Grass Valley Sampling Site Identification

Descriptive		Approx. Distance
Name	Abbreviation	from House (ft)
North Corner	N	10
North Corner Background Collocated	N-B-C	10
Northeast Side Outer	NEO	40
Northeast Side Inner	NEI	5
East Corner	E	10
South Corner	S	10
Southeast Side Inner	SEI	5
Southeast Side Outer	SEO	40
South Corner Background Collocated	S-B-C	10
Southwest Side Inner	SWI	5
Southwest Side Outer	SWO	40

Table 2 (con.) Grass Valley Sampling Site Identification

Descriptive		Approx. Distance
Name	Abbreviation	from House (ft)
West Corner	W	10
Northwest Side Outer	NWO	40
Northwest Side Inner	NWI	5
Northwest Side Inner Collocated	NWI-C	40
Extra Northeast	XNE	80
Extra North	XN	80
North Inside	NIn	
South Inside	SIn	

Referring to Figure 1 and using the site identifiers listed above, in addition to the samplers recommended by DPR, two samplers were used during the "mechanical vent" (period 8) sampling period and were placed downwind of the structure at a distance of approximately 80 feet.

All samplers were positioned at the same elevation relative to the house. All sampler inlets were approximately five feet (+0.5 feet) above the ground.

The collocated sampler was positioned at the north side of the house (NWI sampling position). Two samplers were placed inside the structure immediately after the house was cleared for re-entry for collection of post-aeration indoor samples. The samplers inside the house were on the north and south sides of the first floor. Background samples were collected at the four corner (second ring) locations for 24 hours prior to the fumigation.

Sampling Periods

The fumigation process for powderpost beetles was expected to consist of a 36 to 72 hour exposure period, followed by a one to two hour mechanical vent period and an eight to forty-eight hour aeration period. The DPR's monitoring recommendation (April 15, 2004 memo, Sanders to Cook) also directed that:

"For both sulfuryl fluoride and chloropicrin, samples should be taken before application, during application (exposure period), during mechanical and tarp removal aeration (alternate Daytime/Overnight sampling according to the duration of aeration), and post aeration for two Daytime/Overnight sampling periods. Additionally, after completion of aeration, two 24-hour samples should be taken at each of two different locations inside the fumigated structure for 48-hours sampling duration (total of four samples inside structure)."

The sampling schedule listed in the monitoring protocol (Appendix I) was provided as a guide. Table 3 lists the actual fumigation test sampling periods. The sample times listed are approximate. Refer to the field log sheets for the exact start and stop times for each sample. All times are in Pacific Standard Time (PST).

Table 3
Grass Valley Fumigation Test Sampling Periods

Approx. # Hours	<u>Date</u>	Approx. Time
24 hours	7/18-19/04	0850 to 0850
6.25 hours	7/19/04	1240 to 1830
11.5 hours	7/19-20/04	1830 to 0605
12.5 hours	7/20/04	0605 to 1835
11.5 hours	7/20-21/04	1835 to 0605
12.5 hours	7/21/04	0605 to 1830
11.5 hours	7/21-22/04	1830 to 0605
6 hours	7/22/04	0605 to 1200
1.5 hours	7/22/04	1200 to 1340
5 hours	7/22/04	1340 to 1830
11.5 hours	7/22-23/04	1830 to 0600
12.5 hours	7/23/04	0600 to 1830
11.25 hours	7/23-24/04	1830 to 0540
12.75 hours	7/24/04	0540 to 1830
	24 hours 6.25 hours 11.5 hours 12.5 hours 11.5 hours 12.5 hours 11.5 hours 11.5 hours 6 hours 1.5 hours 1.5 hours 1.5 hours 1.5 hours 11.5 hours	24 hours 7/18-19/04 6.25 hours 7/19/04 11.5 hours 7/20/04 12.5 hours 7/20-21/04 12.5 hours 7/21/04 11.5 hours 7/21-22/04 6 hours 7/22/04 1.5 hours 7/22/04 5 hours 7/22/04 11.5 hours 7/22-23/04 12.5 hours 7/23/04 11.25 hours 7/23-24/04

The house was fumigated at 1215 on July 19, 2004. Mechanical venting started at 1220 and ended at 1343 on July 22, 2004 (includes tarp removal). Due to the length of time required for sample change-out the actual sampling period was longer than the mechanical vent period. Aeration lasted for approximately 20 hours.

Meteorological Monitoring

The meteorological station (oriented toward true north) was positioned 100 feet to the southwest of the southwest corner of the house. The meteorological station was set up, at a height of 21 feet, to determine wind speed and direction, air temperature, barometric pressure and relative humidity. The raw meteorological station data are available in comma delimited text format. Appendix V (page 79 of the Appendices) lists the meteorological station data in 1-minute averages for the "mechanical vent" test period. Appendix VI (page 84 of the Appendices) lists the meteorological station data in 5-minute averages for the remainder of the test period. ARB staff noted the degree of cloud cover on the sample log sheet whenever sample cartridges were changed.

IV. <u>Sampling Procedures</u>

Air sampling for sulfuryl fluoride and chloropicrin was conducted with sampling tubes. For <u>sulfuryl fluoride</u>, the tubes were 8 mm x 110 mm, coconut shell charcoal with 800 mg in the primary section and 200 mg in the secondary (SKC special order). For <u>chloropicrin</u>, the tubes were 8 mm x 140 mm, XAD-4 with 400 mg in the primary section and 200 mg in the secondary (SKC special order).

Sample collection for sulfuryl fluoride was conducted at a flow rate of 50 standard cubic centimeters per minute (sccpm). For chloropicrin, a flow rate of 100 sccpm was used.

Two sulfuryl fluoride cartridges in series were used for sample collection at seven sites (downwind) during the "mechanical aeration" sampling period. Doubling of the cartridges during the mechanical vent period was intended as a precaution to address possible breakthrough at higher concentrations.

Each sample train consisted of an adsorption tube, Teflon® fittings and Tygon® tubing, rain/sun shield, needle valve, train support and a 12 volt DC vacuum pump (Figure 3). Tubes were prepared for use by breaking off the sealed glass end and immediately inserting the tube into the Teflon® fitting. The tubes were oriented in the sample train according to a small arrow printed on the side indicating the direction of flow. Needle valves with a range of 0-100 ccpm and 50-500 ccpm were used to control sample flow for sulfuryl fluoride and chloropicrin sampling, respectively. The flow rates were set using calibrated digital mass flow meters (MFM) before each sampling period. A MFM scaled from 0-200 sccpm was used for both sulfuryl fluoride and chloropicrin samplers. The flow rate was also checked and recorded, using the MFM, at the end of each sampling period. Any change in flow rates was recorded on the field log sheet. The pesticide sampling procedures for adsorbent tubes are included in Appendix I (page 25 of Appendices).

Immediately after sampling, the tubes were capped, labeled, placed in a culture tube and stored and transported in an insulated container with dry ice to the ARB laboratory in Sacramento.

Caution was used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

V. Analytical Methodology

The sampling and analysis method (SOP) and validation results for sulfuryl fluoride are included in Appendix I. The sulfuryl fluoride method consists of sampling with charcoal cartridges at a flow rate of 50 sccpm followed by extraction with 40 millimolar sodium hydroxide and anion exchange ion chromatography. The DPR recommended a target 24-hour estimated quantitation limit (EQL) of 30 ug/m³ for sulfuryl fluoride. The SOP specifies an EQL of 11.5 ug/sample, which corresponds to 160 ug/m³ for a 24-hour sample collected at 50 sccpm. With respect to sample stability, analytical validation work conducted prior to the study indicated that sulfuryl fluoride samples are stable for at least six weeks. All sample analyses for sulfuryl fluoride were conducted with a six-week timeframe.

The SOP for chloropicrin is included in Appendix I. The chloropicrin method consists of sampling with XAD-4 cartridges, extraction with three milliliters of methylene chloride and analysis using gas chromatography/mass selective detector operated in the selected ion-monitoring mode. The DPR recommended a target 24-hour EQL of 0.1 ug/m³ for chloropicrin. The SOP specifies an EQL of 19.8 ng/sample, which

corresponds to 138 ng/m³ (0.138 ug/m³) for chloropicrin for a 24-hour sample collected at 100 sccpm. Analytical method validation work conducted prior to the study indicated that chloropicrin stability was within acceptable limits for at least six weeks. All sample analyses for chloropicrin were conducted with a six-week timeframe.

VI. Monitoring Results

A total of 179 samples each (including background and collocated samples; excluding spikes and blanks) were collected for sulfuryl fluoride and chloropicrin. Two sulfuryl fluoride samples (log #30 and #145) and one chloropicrin sample (log # 29) were invalidated due to field collection problems or laboratory processing issues.

Sample results for sulfuryl fluoride and chloropicrin are discussed below. Tables 5 and 8 of this report present the results of air monitoring for sulfuryl fluoride and chlorpicrin in units of ug/m³ and ng/m³, respectively, and in units of parts per billion by volume (ppbv) and parts per trillion by volume (pptv), respectively. A summary of the sulfuryl fluoride and chloropicrin results are presented in Tables 6 and 9, respectively. A summary of the sulfuryl fluoride and chloropicrin results are also presented in Figures 4 through 16 and 17 through 29, respectively, as associated with wind roses for each sampling period.

Laboratory results are reported to three significant figures and the sample results (in air concentration units) equal to and above the estimated quantitation limit (EQL) are reported to two significant figures. Results equal to or above the method detection limit (MDL) but less than the EQL are reported as "detected."

Sulfuryl Fluoride

The outdoor sulfuryl fluoride results ranged from <MDL to 100,000 ug/m³ (24,000 ppbv). The highest outdoor concentration was observed at a sampling site on the opposite side of the house but downwind from the mechanical vent during the mechanical vent sampling period (period eight). The test results are shown in a bar graph included in the executive summary.

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable levels (>EQL) were also observed during all of the fumigation exposure periods. Four samples had a quantifiable results during the first aeration sampling period (period nine) and only one sample had a quantifiable level observed during the remaining aeration periods (ten through thirteen).

The laboratory report states: "Because all system blanks were <MDL and most extraction blanks were DET it seems probable that the charcoal collection tubes contain a small amount of fluoride. Blank values were not subtracted from the monitoring data." Thus, all "detect" results from this study should be considered as questionable due to low level contamination. Since quantifiable results (i.e., above the EQL) were not found in any cartridge (extraction) blanks, the sample results above the EQL should not be considered as affected by this low level contamination issue.

We collected 179 samples for sulfuryl fluoride (includes four background samples and 13 collocated samples). Of those, 63 sample results were found to have quantifiable concentrations above the EQL, 68 sample results were "detected", 46 sample results were <MDL, and two sample results were invalid (log #s 30 and 145). The sulfuryl fluoride results from three of the background samples were <MDL and the north site was "detected."

Backup cartridges (a second cartridge in series behind the primary cartridge) were collected at seven sites during the "mechanical vent" period. Of the seven backup cartridges collected, none had a quantifiable result above the EQL.

Two sequential 24-hour samples were collected inside the house at two locations (north and south ends of the first floor) after the end of the aeration period. The sulfuryl fluoride results of the north inside sampler were 1600 (390 ppbv) and 750 ug/m³ (180 ppbv), respectively, for the two sequential 24-hour samples. The sulfuryl fluoride results of the south inside sampler were 2400 (570 ppbv) and 1100 ug/m³ (270 ppbv), respectively, for the two sequential 24-hour samples.

No sample results have been adjusted or corrected for recoveries of quality assurance spike samples. Analytical method validation prior to the study demonstrated that sulfuryl fluoride samples were stable over the time period covering sample collection, transport, storage, and analysis.

Chloropicrin

The outdoor chloropicrin results ranged from <MDL to 43,000 ng/m³ (6400 pptv). The highest outdoor concentration was observed at a sampling site on the opposite side of the house but downwind from the mechanical vent during the mechanical vent sampling period (period eight). This site and sampling period also had the highest level of sulfuryl fluoride. The test results are shown in a bar graph included in the Executive Summary.

In general, the highest concentrations were observed during the mechanical vent period. Quantifiable results (>EQL) were observed during all of the fumigation exposure periods. A total of four samples had quantifiable results during the first two aeration sampling periods (periods six and seven) and no quantifiable levels were observed during the remaining aeration periods, eight and nine.

Of the 179 samples collected for chloropicrin (includes four background samples and nine collocated samples), 97 sample results were found to have quantifiable concentrations above the EQL, 43 sample results were "detected," 38 sample results were <MDL and one sample was invalid.

Four samples were collected for the background period (i.e., prior to application) from the east (E), north (N), south (S) and west (W) sites. The chloropicrin results from the four background samples were all <MDL.

Two sequential 24-hour samples were collected inside the house at two locations (north

and south ends of the first floor) after the end of the aeration period. The chloropicrin results of the north inside sampler were 72,000 (11,000 pptv) and 47,000 ng/m³ (7000 pptv), respectively, for the two sequential 24-hour samples. The chloropicrin results of the south inside sampler were 83,000 (12,000 pptv) and 53,000 ng/m³ (7900 pptv) respectively, for the two sequential 24-hour samples. It should be noted that these indoor concentrations of chloropicrin following aeration were higher than were measured outdoors during mechanical venting. It should also be noted that the acute (1-hour) reference exposure level established by the Office of Environmental Health Hazard Assessment (OEHHA) for chloropicrin is 29,000 ng/m³ (toxicity endpoint is mild eye and respiratory irritation).

No sample results have been adjusted or corrected for recoveries of quality assurance spike samples. Refer to Section VIII below for details on chloropicrin breakthrough.

VII. Field Quality Control

Field quality assurance for the application monitoring included the following:

- Two field spikes for chloropicrin obtained by sampling ambient air at the application monitoring site. The field spikes were obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample).
- 2) Two field spikes for chloropicrin and two dynamic field spikes (see page 13 for description) for sulfuryl fluoride collected by sampling ambient air at the ARB 13th and T facility.
- 3) Four trip spikes each for sulfuryl fluoride and chloropicrin. The trip spikes were labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.
- 4) Four lab spikes prepared at the same level as the field and trip spikes.

 The lab spikes remained in the laboratory freezer and were extracted and analyzed along with the field and trip spikes.
- 5) Collocated (replicate) samples taken for all sampling periods (except the background period) at one sampling location (NWI).
- 6) One trip blank each for sulfuryl fluoride and chloropicrin. Each trip blank was obtained, labeled, recorded on the field log-sheet, and transported and submitted along with the field and trip spikes and application samples.
- 7) The battery operated mass flow meters used to set and check the sampling flow rate were calibrated by the ARB's Quality Assurance Section

VIII. Quality Control Results

A. Trip Blanks

The result for the sulfuryl fluoride trip blank was "detected". The result for the chloropicrin trip blank was <MDL.

B. Collocated Sample Results

The relative percent difference (RPD) of the collocated results provides an indication of the precision of the monitoring method (i.e., the lower the RPD the better the precision). RPD is calculated as follows: RPD=(| difference |/average) x 100.

Referring to Table 7, seven collocated pairs of samples for the fumigation study had collocated sulfuryl fluoride results above the EQL. The RPD of the data pairs ranged from 2 percent to 35 percent, with an average of 17 percent, indicating acceptable precision for the sampling and analyses.

Referring to Table 10, nine collocated pairs of samples for the fumigation study had collocated chloropicrin results above the EQL. The RPD of the data pairs ranged from 0 percent to 36 percent, with an average of 11 percent, also indicating acceptable precision for the sampling and analyses.

C. Laboratory, Trip and Field Spikes

The purpose of collecting spiked samples is to assess the accuracy (percent recovery) of the sampling and analytical methods. Laboratory, trip, and field spikes were prepared by spiking a known amount of the target compound onto the appropriate cartridges. The field spikes are normally collected by sampling ambient air through the previously spiked cartridges at one of the sampling sites during the background sampling. Thus, the field spikes provide an assessment of the accuracy of the entire method and are collected under the same environmental and experimental conditions as those occurring at the time of ambient sampling. The lab and trip spikes are used to confirm the field spike results or to help identify the source of losses (or other problems) when they occur in the field spikes.

The laboratory spikes were immediately placed in a freezer and kept there until extraction and analysis. The trip and field spikes were kept in the lab freezer until transported to the field. The trip spikes were kept on dry ice in an ice chest (the same one used for samples) during transport to and from the field and at all times while in the field except log-in and labeling. The extraction and analysis of each set of laboratory, trip and field spikes normally occurs at the same time. The collocated (unspiked) background sample result, if above the EQL, is subtracted from the field spike sample result before calculation of percent recovery of the analytes.

The lab, trip and field spike results (average percent recovery) are summarized in Table

4 and discussed below.

Table 4
Spike Results
Average Percent Recovery

	Sulfuryl Fluoride	Chloropicrin
Lab	89	88
Trip	90	84
Field	91	79

Sulfuryl Fluoride: The sulfuryl fluoride laboratory, trip and field spike results for the fumigation study are listed in Tables 11, 12, and 13, respectively. Each of the lab and trip spike cartridges was spiked with 54.8 ug/sample of sulfuryl fluoride.

For sulfuryl fluoride, method development work showed that use of a dynamic spiking procedure was necessary in order to accurately reflect sampling conditions (i.e., to generate field spikes) for sulfuryl fluoride in ambient air. The dynamic spiking system mixes a known volume of standard gas, from a certified gas standard, with ambient air prior to passing into the sampling cartridge. Thus, a known concentration of sulfuryl fluoride in ambient air is generated that can be sampled through a charcoal cartridge for the sampling duration and at the sampling flow rate used for fumigation tests. However, it is not generally feasible to run the dynamic field spike procedure at the application test sites. For this test, daytime and overnight dynamic field spikes were generated, for two 24-hour periods (4 samples) at the ARB 13 and T Street facility during the time that the test in Grass Valley was being conducted. The first two field spikes were collected from 7/18/04 to 7/19/04 and the second two from 7/19/04 to 7/20/04. The sampling periods were approximately 12 hours each.

The concentration of the sulfuryl fluoride gas standard used was 137,400 micrograms per cubic meter (ug/m³)(33.0 ppmv; Scott Marrin, 3/21/01, \pm 2%). By adding two (2) sccpm of standard gas into 48 sccpm of ambient air for a total sampling flow rate of 50 sccpm, the resulting sulfuryl fluoride concentration was calculated as 5,496 ug/m³ (i.e., 2/50 x 137,400 ug/m³ = 5,496 ug/m³). The approximate expected amount of sulfuryl fluoride spiked onto the cartridges, using this approach, for a 12-hour sample is 198 ug. The exact amount per cartridge varied slightly depending on the exact duration of each sample collection.

The average recovery of the four field spikes was 91 percent. The field spike results are consistent with the lab and trip spike results and indicate that the sampling, sample transport, storage and analytical procedures used in this study produce acceptable results for sulfuryl fluoride.

Chloropicrin: The chloropicrin laboratory, trip, and field spike results for the fumigation study are listed in Tables 14, 15, and 16, respectively. Each of the spike cartridges was spiked with 228 ng/sample of chloropicrin. Two of the field spikes were collected at the

test site and two were collected at the same time as the dynamic spikes collected for sulfuryl fluoride at the ARB 13th and T Street facility. Breakthrough of chloropicrin from the primary XAD-4 bed to the secondary bed in the cartridges occurred for all four field spikes. The results reported in Table 16 for the field spikes are the sum of the amounts measured in the primary and secondary beds. Although no definite explanation can be provided for the breakthrough, it may be attributable to the spiking process (syringe injection partially into the primary bed) and the relatively high ambient temperatures during the study period. The field spike results are consistent with the lab and trip spike results and indicate that the sampling, sample transport, storage and analytical procedures used in this study produce acceptable results for chloropicrin.

D. Breakthrough

The following is in reference to the evaluation of samples collected in the field for breakthrough. See laboratory reports in Appendix for additional details.

Sulfuryl Fluoride: A subset of samples collected during period eight (mechanical vent), which included samples 106 through 115, were evaluated for breakthrough. These samples were collected using two charcoal tubes in series. All the primary beds from the back tubes were analyzed and showed no quantifiable amounts of sulfuryl fluoride. For those samples that had quantifiable levels in the primary bed of the front tube, the secondary bed in the front tube was analyzed and no quantifiable sulfuryl fluoride was detected. In addition, the secondary bed of a select group of samples other than those in period eight (i.e., samples 116, 117, 162, 163, and 190) were analyzed and found to have no quantifiable amounts of sulfuryl fluoride. These results indicate that breakthrough was not a problem in this study.

Chloropicrin: A total of 179 application samples were analyzed for chloropicrin. Six samples (26, 28, 157, 158, 172, and 173) were found to have levels beyond the high calibration point of the analytical instruments. The back sections of these collection tubes were analyzed. High levels of chloropicrin were found in four of the six samples (157, 158, 172, and 173), which were all collected inside the structure. The exact reason for the breakthrough with these four samples remains unknown, but may have been due to temperature in the field or other factors.

To evaluate if breakthrough occurred during the collection of other samples, an additional group of 12 samples was chosen at random and their secondary beds were analyzed. The primary bed concentrations in these samples ranged from 72 to 681 ng/sample. Chloropicrin was not detected in any of the secondary beds of these 12 samples.

Figure 1
Grass Valley Fumigation Site Map

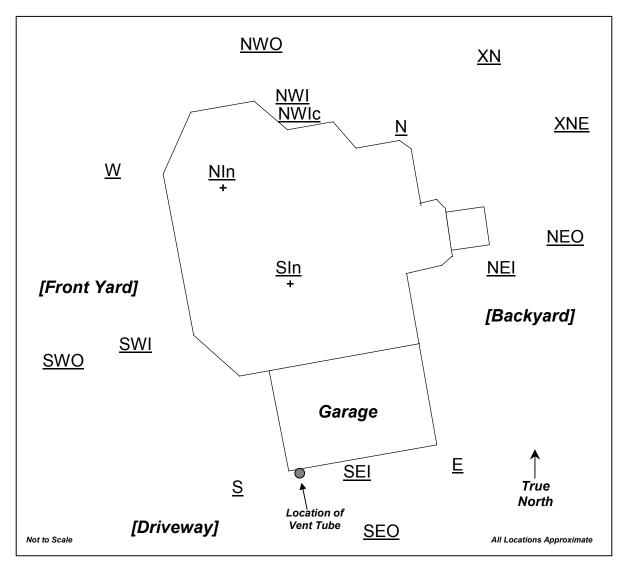


Figure 2
Grass Valley Fumigation Site Diagram

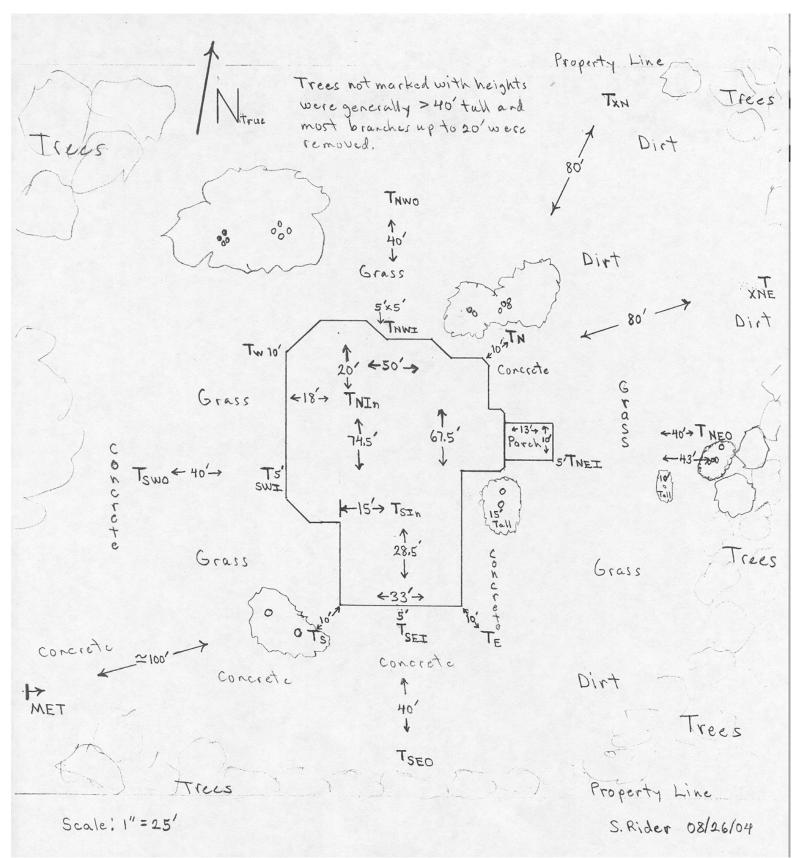


Figure 3
Cartridge Sampling Manifolds

